UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION DIVISION
P.O. BOX 1198, ADA, OK 74821

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OFFICE OF
RESEARCH AND DEVELOPMENT

MEMORANDUM

SUBJECT: Olin Chemical Superfund Site (Wilmington MA) (19-R01-005)

FROM: Scott G. Huling, Environmental Engineer
Applied Research and Technical Support Branch

TO: Melanie Morash, Remedial Project Manager
James DiLorenzo, Remedial Project Manager
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A technical review has been completed regarding the Technical Memorandum regarding "Olin DAPL – Wastewater Treatment Approach" (by Wood Environment & Infrastructure Solutions, July 31, 2019). Two of the five proposed treatment options have been retained for further consideration. The treatment option 3.2.4. Chrome Removal, Metal, Sulfate and Ammonia Removal Prior to Evaporation, involves the widest integration of treatment technologies and addresses key environmental parameters in the wastewater stream. A second, less comprehensive treatment option was also retained for further evaluation but requires some clarification regarding details.

It is assumed that a small-scale pilot study may eventually be deployed involving various treatment technologies in a treatment train configuration. An important element in the success of the wastewater treatment pilot-study is to acquire a dense aqueous phase liquid (DAPL) wastewater stream that exhibits nearly constant physical and chemical characteristics throughout the testing period. This may be challenging, however, in a previous technical review memorandum (November 16, 2018), it was recommended to install a groundwater extraction well designed with a short well screen specifically to remove the DAPL and to minimize the disturbance of the overlying DAPL-groundwater interface. The technical review memorandum has been included as an attachment. It is recommended to consider using an extraction well designed in this manner to provide DAPL for the pilot-scale testing.

Dr. Klara Rusevova (National Research Council, Ada, OK) assisted in this technical review. If there are questions, or if additional assistance can be provided, please call me (580) 436-8610.

Attachment

cc: Lynne Jennings, Region 1
Bill Brandon, Region 1
Jan Szaro, Region 1
James Cummings HQ
Ed Gilbert, HQ
David Bartenfelder, HQ
Linda Fiedler, HQ

Technical Review Comments and Recommendations.

General Comments.

1. It is assumed that a small-scale pilot study may eventually be deployed involving various treatment technologies in a treatment train configuration. A key element in the success of the wastewater treatment pilot-study is to acquire a dense aqueous phase liquid (DAPL) wastewater stream that exhibits nearly constant physical and chemical characteristics throughout the testing period. The DAPL/groundwater extraction step component of the proposed pump and treat process was not presented in the technical memorandum. In a previous memo (November 16, 2019), comments and recommendations were provided that outlined an explanation for the "failure" of the previous DAPL removal pilot test, and a potential alternative design involving a short-screened extraction well that could be used to remove the DAPL. The objectives of the alternative well design were to allow multiple wells to operate simultaneously, minimize disturbance of the DAPL, achieve a uniform decline in the DAPL pool, and to optimize/shorten the time of recovery of the DAPL groundwater. It is recommended to construct the well so it could be used to provide DAPL during the proposed wastewater treatment pilot test outlined in the technical memorandum.

2. The disposal, or disposition of the treated water was not proposed and discussed (i.e., re-injected, sanitary sewer, NPDES, etc.). It is recommended to identify various disposal options and applicable treatment requirements, if known, to further assess whether the proposed treatment train is sufficient, or whether additional treatment may be needed.

Specific Comments.

Section 1.5 Wastewater Analysis.

1. The summary of wastewater analysis provides a good overview of the wastewater treatment challenges. One challenge is to remove chromium species prior to advanced oxidation processes and ammonia stripping (i.e., aeration) to limit the potential for Cr^{+3} oxidation to Cr^{+6}. The abundance of organic carbon (430-2900 mg/L) provides oxidizable material that will compete with target compounds, i.e., NDMA, when deploying advanced oxidation processes (AOPs); and the high concentrations of Cl^{-} and Br^{-} represent radical scavengers when deploying AOPs. These are two potential sources of treatment inefficiency.

2. It was reported that, "Based on theoretical solubility limits these maximum chloride and sulfate concentrations cannot be as reported unless salt crystals were observed; the associated samples were free of precipitated solids." The DAPL analysis reports high suspended solids (840-95,700 mg/L) suggesting that salt crystals may potentially have been present.

3. Ideally, during the proposed precipitation processes, it may be possible to achieve gratuitous solids and dissolved constituent removal as a result of various mechanisms including precipitation, coagulation, flocculation, agglomeration, electrostatic attraction, adsorption, etc. This underscores to importance of the proposed hydroxide-based precipitation treatment process.

Section 2.1 Reduction of Hexavalent Chromium to Trivalent Chromium.

The reaction involving NaOH was not balanced and has been balanced below. This indicates that greater stoichiometric quantity of NaOH will be needed (i.e., 6 moles NaOH) for Cr^{+3} precipitation.

$Cr_2(SO_4)_3 + 6\ NaOH \rightarrow 2\ Cr(OH)_3\ (s) + 3\ Na_2SO_4$
$Cr_2(SO_4)_3 + 3\ Ca(OH)_2 \rightarrow 2\ Cr(OH)_3\ (s) + 3\ CaSO_4$

Section 2.2 Advanced Oxidation.

1. The report correctly points out the challenges of radical based oxidative treatment. There are other key factors to consider. The wastewater analysis indicates that a wide range in iron (3.3-3600 mg/L) and manganese (0.72 – 700 mg/L) concentrations in the DAPL. It is unclear what the role the precipitation treatment step will have on the fate of these metals in the wastewater. However, it is safe to assume that some removal will be achieved. Residual iron remaining in the wastewater effluent, i.e., from lime treatment, may potentially serve as a catalyst for the AOP (i.e., assuming Fenton reaction ($Fe^{+2} + H_2O_2$), as proposed. However, some iron oxides, in addition to most manganese-based mineral species are involved in non-productive reactions (NPR) where H_2O_2 disproportionation occurs yielding $H_2O + O_2$ without hydroxyl radical (•OH) production. The lime precipitation treatment process will likely remove Fe and Mn and will help limit this potential source of inefficiency.

2. The balanced reactions involving Cr^{+3} and Cr^{+6} should be scrutinized as far as establishing a correlation between lime requirements and Cr removal. Other dissolved species will be unstable at pH 8 and significant precipitation will likely occur when the acidic wastewater is neutralized.

Section 2.3 Removal of Ammonia.

The dissolved ammonium ions can be converted to ammonia gas and stripped from the water to the air. It was proposed that the stripped ammonia would have to be captured and acid scrubbed with sulfuric acid to produce ammonium sulfate solids, which would complicate the treatment system, and create residuals to manage. Specifically, the acidic ammonium sulfate slurry would have to be sent off site for disposal.

Ammonia gas (NH_3) is a greenhouse gas and its release may not be appropriate. Given the very high ammonia concentrations found in the DAPL, and the volume of water being treated, this could account for a large CO_2-equivalence footprint. Based on a preliminary literature search, there appears to be a biological treatment option that may serve a useful purpose, be greener, and potentially avoid the acidic ammonium sulfate slurry disposal issue. Dissolved organic residuals present in the waste stream may serve as an electron donor and support a biological treatment process. It is recognized that the concentration of NH_3 in the waste stream is significant, and the transport and fate of NH_3 in any treatment process represents a unique challenge. In general, it is recommended that the general feasibility of greener treatment technologies be evaluated to assess the feasibility of treating ammonia gas residuals in the waste stream.

Clemens, J., Cuhls, C. 2003. Greenhouse gas emissions from mechanical and biological waste treatment of municipal waste. *Environ Technol.* 24 (6):745-54.
Kanagawa, T., Qi, H.W., Okubo, T., Tokura, N. 2004. Biological treatment of ammonia gas at high loading. *Water Sci Technol.* 50 (4):283-90.

Section 3.2.1. Metal Removal Prior to Evaporation.

1. Section 2.1 reported that the DAPL chemistry data indicates that the chromium in the DAPL is in the Cr^{+3} form and that reduction of Cr^{+6} to Cr^{+3} is not a necessary treatment step as trivalent chromium can be removed using conventional hydroxide precipitation processes. However, in this section it is proposed to include a reduction step (Cr^{+6} to Cr^{+3}). It may have been assumed that some Cr^{+3} may be oxidized during the extraction step. Please clarify.

2. It does not appear that ammonia removal is a component of this treatment train. This limitation was not addressed in the effectiveness summary (see section 2.3, above).

3. The proposed caustic treatment appears to involve NaOH and not lime. Given the advantages of lime versus NaOH caustic treatment (Table 3), lime treatment appears to be more advantageous. Please clarify why NaOH is being proposed.

Section 3.2.2 Sulfate, Organics and Ammonia Removal Prior to Evaporation.

It was assumed in this treatment approach that the microfiltration step would significantly remove Cr species. Assuming it does not, the use of AOP and ammonia stripping (i.e., aeration) may oxidize Cr^{+3} to Cr^{+6}, which is not recommended. Consequently, stabilization of sludge from the microfiltration step may help precipitate and immobilize Cr in the sludge but would leave Cr residuals in the wastewater effluent. In general, 3.2.2 does not appear to be a top candidate for further evaluation. This was the conclusion stated in this section (i.e. “Wood does not recommend further evaluation for this option), but later in section 4.0 it was retained for further evaluation. Please clarify.

Section 3.2.4. Chrome Removal, Metal, Sulfate and Ammonia Removal Prior to Evaporation.

This treatment option involves the widest integration of treatment technologies and addresses key environmental parameters in the wastewater stream.

Section 4.0 Conclusion.

1. It was reported that treatment options 3.2.2 and 3.2.4, outlined in Section 3, be retained for further consideration. However, it was reported in section 3.2.1 that this option appears feasible and should be carried forward; and in section 3.2.2 that the treatment option was not recommended for further evaluation. Consequently, it appears that the two options considered for further evaluation should be 3.2.1 and 3.2.4. Please clarify.

2. In general, option 3.2.1 appears to be more feasible than 3.2.2, but less feasible than 3.2.4. The basis for this observation is that in 3.2.2, lime stabilization occurs after microfiltration and AOP treatment. Ideally, lime treatment will result in significant precipitation in the complex mixture and may remove a wide range of DAPL constituents listed in Tables 1-2. Post-precipitation AOP deployment has a better chance of being effective by eliminating various sources of treatment inefficiency including non-productive reactions and scavengers (discussed above). Conversely, 3.2.1 does not involve HDS treatment nor ammonia treatment. Inclusion of these treatment options in the overall process, as proposed in 3.2.4, are key elements in the overall treatment train. Contrasting results from 3.2.1 and 3.2.4 will empirically reveal the collective effects of (A) the reduction step on Cr^{+3} removal, (B) the effects of NaOH versus lime treatment on the precipitation mechanism and residuals remaining, and (C) the effects of ammonia treatment.

3. The description of 3.2.4 in this section includes the reduction step (proposed in 3.2.1, but not in 3.2.4). Please clarify if this step is included in 3.2.4.

Attachment – Technical Review Memorandum (November 16, 2018) from Scott G. Huling, Office of Research and Development, Groundwater and Ecosystem Restoration Division (Ada, OK), to James DiLorenzo and Christopher Smith, Remedial Project Managers, US EPA, Region 1 Boston MA 02109.